

Evolution of Boron K Near Edge Structure in Ultra-Short Period W/B₄C Multilayers: Differences in Transmission and Photocurrent Measurements

C. C. Walton and J. B. Kortright
Materials Science Division
Ernest Orlando Lawrence Berkeley National Laboratory
Berkeley, California, 94720 USA

INTRODUCTION

In a larger study of the microstructure/performance relationships of ultra-thin W/B₄C multilayer x-ray interface structures,¹ we measured near-edge absorption spectra across the B K edge for multilayer periods ranging from 5-50 Å. Near-edge absorption measurements were chosen because of their potential sensitivity to changes in local bonding environment² that might shed light on questions concerning the changing extent of intermixing between the W- and B₄C-rich layers as a function of multilayer period. Absorption spectra were collected in both transmission and photocurrent modes for samples with a range of multilayer periods and for pure B₄C films. While subtle, systematic changes were observed between samples, very significant differences were observed between transmission and photocurrent data sets, which are clearly the result of bulk vs. surface sensitivity, respectively, of the different measurement techniques. These results thus have important implications for ALS experimenters whose goal is to study soft x-ray absorption features from the bulk of samples.

EXPERIMENT

The multilayers were deposited by conventional magnetron sputtering techniques at the Center for X-Ray Optics, LBNL, on Si₃N₄ membranes about 1500Å thick. The number of periods was adjusted for a constant overall thickness of the multilayer of another 1500Å, to give an absorption drop near 1/*e* at the B edge (188eV). Absolute transmission was measured by a GaAs photodiode behind the sample, and electron total yield (photocurrent) with a Keithley picoammeter attached to the samples, otherwise electrically isolated.

RESULTS

Absolute absorption measurements were normalized with the I_0 of the full incident beam, then plotted as $\mu \propto -\ln(I/I_0)$ to show the edge as an increase in absorption. Both measurements were also normalized by the photocurrent from the beamline M3 mirror to remove the decay of the beam over time. The curves have been scaled to show the same change in height from 180eV to 220eV, and have been displaced vertically by arbitrary factors for comparison.

DISCUSSION

For both techniques, only subtle changes with multilayer period are observed. A π^* shoulder near 192eV is seen in all the curves and does not change much with period. The curves also show a broad σ^* feature near 200eV which shows a slight narrowing as the period decreases. The most distinct difference between any of the curves is the sharp peaks appearing for all samples in the photocurrent measurements, which are totally absent in the transmission measurements. Since the measurements were made during the same experiment the difference cannot be attributed to any change of the specimens over time. However, the two techniques are quite different in their surface sensitivity. The photocurrent measures only those electrons which escape the sample completely, so it is dependent on the energy distribution of the excited electrons and their proximity to the

surface. The energy distribution is complex, with contributions from photoelectrons and secondary and Auger electrons, but is dominated by a low-energy tail below 20eV. Since these electrons have escape depths from a few atomic diameters to 50Å, the photocurrent represents absorption by atoms very near the surface. By contrast the transmission measurement averages through the bulk of the specimen.

Similar photocurrent measurements by Jia³ on a variety of metal borides show peaks at 193.9eV, very close to the peak at 193.8eV in this study. Results by Jia³ on several other B compounds also show this peak, and it appears most strongly in a specimen of B₂O₃. Its presence in every scan suggests that surface oxidation of the specimens is responsible. A peak at 192.3eV in B compounds has been identified Chaiken and Terminello⁴ as a quasi-bound π^* state consistent with an sp² bonding state of B, and is absent in the case of full sp³ hybridization.

The absence of these sharp peaks in our transmission results suggests they result from a surface phase that is too thin to give a significant signal above the bulk. The multilayers are expected to contain a highly disordered bonding state of the B atoms, since they are amorphous sputtered layers of high-melting-point compounds that have strong chemical bonding and little mobility on the growing film surface. The sharp peaks in the photocurrent results are consistent with a better-defined chemical state, such as might be formed in an equilibrium process like surface oxidation. Based on the signal-to-noise ratio of the absorption measurement and the maximum contribution from the surface phase that would not appear above the noise, the thickness of the surface phase can be estimated as 50Å or less, consistent with the escape depth available to the electrons giving the sharp peaks in the TEY results.

In the transmission absorption results, several trends with d-spacing can be observed. A subtle pre-edge feature at 189eV (which can be elaborated in a derivative plot) becomes stronger with shorter multilayer period. The π^* feature at 192eV also becomes stronger with shorter period, measured as absolute height or relative to the post-edge jump height at 220eV. Third, the broad σ^* feature changes shape with decreasing period, from a broader, two-lobed shape similar to that in B₄C, at d = 30Å, to a narrower single-lobed shape at d = 6Å.

The stronger π^* feature is consistent with more unhybridized p-orbitals as the layers get thinner. Microstructural studies by HRTEM show that the thinner B₄C layers are more mixed with the adjacent W layers. Since W forms very stable borides and carbides it is reasonable to expect more bonding with W to introduce some d-character in the boron bonding environment, which would reduce the sp³ hybridization in B₄C. This is also consistent with the σ^* feature evolving to a different shape from that found in B₄C. Further study including single films of WB and WB₂, the expected end products of increasing intermixing at the mole ratios present, would allow more a conclusive interpretation.

CONCLUSIONS

The transmission absorption spectra show changes consistent with a greater degree of intermixing with shorter multilayer period. Though the multilayers retain separate W-rich and B-rich phases even at the shortest periods, as demonstrated in other parts of this study,¹ the thinner layers and greater interface area in the thinner layers cause a closer average proximity of W and B atoms. These trends in the boron bonding can be observed with a relatively simple experiment, though a fuller set of standard specimens is needed for a more complete interpretation.

Distinct differences between boron K-edge absorption spectra taken by transmission or by photocurrent show that the high surface sensitivity of the photocurrent measurement can significantly distort the results, which should not be interpreted as representing the bulk without careful consideration of the sampling depth and possible surface contamination.

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Author Affiliations:

contact author: CCW now at Advanced Microtechnology Program, L-395, Lawrence Livermore National Laboratory, Livermore, CA 94550 USA. e-mail walton9@llnl.gov, phone 510-423-2834.

PI when experiments were done: JBK at Materials Science Division, MS 2-100, Lawrence Berkeley National Laboratory, Berkeley, CA 94720. e-mail jbkortright@lbl.gov, phone 510-486-5960.

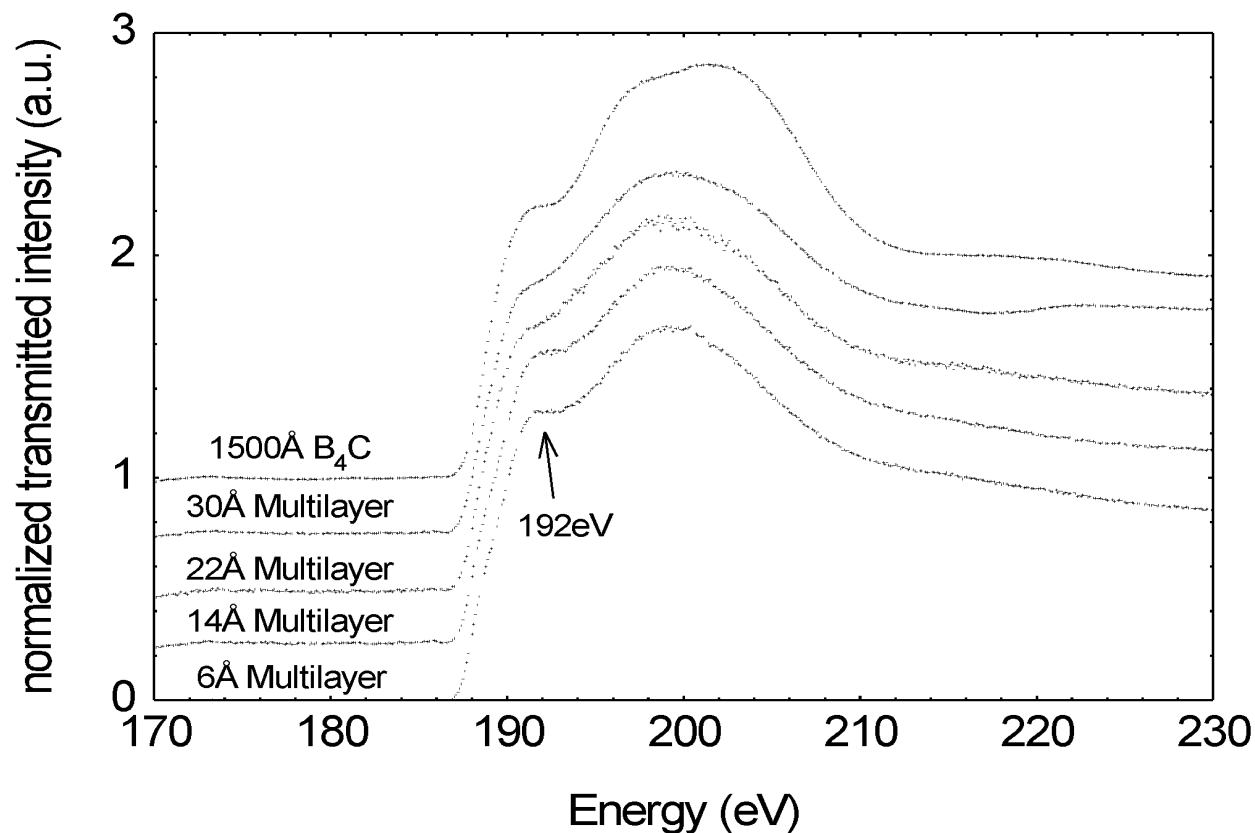


Fig. 1. Near-edge absorption spectra at the boron K edge (188 eV) of four W/B₄C multilayers and of a single film of B₄C, measured in transmission. Note smooth curves near the edge, despite the high energy resolution of the measurement (< 0.1 eV). Curves have been displaced vertically for comparison.

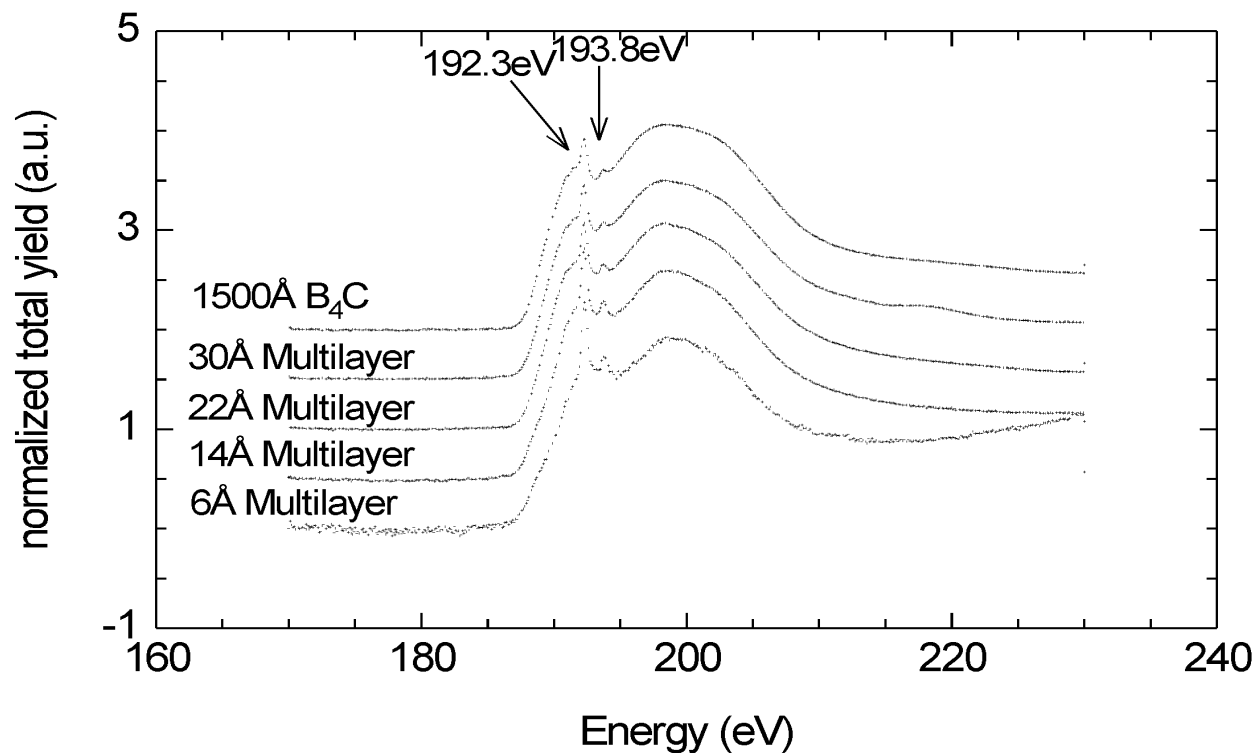


Fig. 2. Same spectra measured by photocurrent, taken in the same experiment as results above. Discrepancy in sharp peaks near the absorption edge underscores high surface sensitivity of the photocurrent measurements.